

## CLAIMS

1. A printing sheet comprising a substrate and, on at least one side of the substrate, an image receptive coating layer with a cumulative porosity volume of pore widths below 200nm as measured using nitrogen intrusion methods of more than  $0.006 \text{ cm}^3$  per gram paper.
2. Printing sheet according to claim 1, characterised in that the cumulative porosity volume of pore widths below 200 nm is more than  $0.008 \text{ cm}^3$  per gram paper.
3. Printing sheet according to one of the preceding claims, characterised in that the surface of the image receptive layer is substantially non-polar.
4. Printing sheet according to claim 3, characterised in that the polar part of the surface energy of the surface of the image receptive layer is less than  $7 \text{ mN/m}$ , preferably less than  $6 \text{ mN/m}$  as determined by contact angle measurements at a Parker Print Surf (PPS) surface roughness of between  $0.8$  and  $1 \text{ }\mu\text{m}$ , preferably of less than  $0.9 \text{ }\mu\text{m}$ , wherein preferentially the polar part of the surface energy of the surface of the image receptive layer is more than  $4 \text{ mN/m}$ .
5. Printing sheet according to one of the preceding claims, characterised by a gloss on the surface of the image receptive coating of more than 75 % according to TAPPI 75deg.
6. Printing sheet according to one of the preceding claims, characterised by a gloss on the surface of the image receptive coating of more than 45, preferably more than 50 according to DIN 75deg.

7. Printing sheet according to one of the preceding claims, characterised in that an image receptive coating layer is provided on the both sides of the substrate.
8. Printing sheet according to one of the preceding claims, characterised in that it has a specific volume of more than  $0.8 \text{ cm}^3/\text{g}$ , preferably of more than 0.82 or  $0.85 \text{ cm}^3/\text{g}$ .
9. Printing sheet according to one of the preceding claims, characterised by an ink set-off of less than 0.3 at 30 secs, preferably of in the range of between 0.15 to 0.25 or of approx. 0.2 at 30 seconds.
10. Printing sheet according to one of the preceding claims, characterised in that the image receptive coating layer comprises a top layer (1) comprising:  
a pigment part, wherein this pigment part is composed of
  - a) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than  $1 \mu\text{m}$ , preferably with a particle size distribution such that approximately 90 % of the particles are smaller than  $1 \mu\text{m}$ ,
  - b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 90 % of the particles are smaller than  $1 \mu\text{m}$ , preferably with a particle size distribution that more than 95 % of the particles are smaller than  $1 \mu\text{m}$ ,
  - c) 0 to 20 parts or up to 30 parts in dry weight of a particulate, preferably solid or vacuolated polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than  $0.5 \mu\text{m}$ , preferably with a particle size distribution such that 90 % of the particles have sizes

between 0.05 and 0.3  $\mu\text{m}$ , in particular between 0.1 and 0.2  $\mu\text{m}$ , or in the case of a vacuolated polymer pigment also with a mean particle size of about 0.6  $\mu\text{m}$ ,

and a binder part, wherein this binder part is composed of:

- a') less than 12 to 16 parts in dry weight of binder and
- b') less than 2 parts in dry weight of additives.

11. Printing sheet according to one of the preceding claims, characterised in that the image receptive coating layer comprises a top layer (1) comprising:

a pigment part, wherein this pigment part is composed of

- a) 0 to 50 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,
- b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 90 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution that more than 95 % of the particles are smaller than 1  $\mu\text{m}$ ,
- c) 2 to 100 parts in dry weight of a particulate solid polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than 0.5  $\mu\text{m}$ , preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3  $\mu\text{m}$ , in particular between 0.1 and 0.2  $\mu\text{m}$ ,

and a binder part, wherein this binder part is composed of:

- a') less than 12 to 16 parts in dry weight of binder and
- b') less than 2 parts in dry weight of additives.

12. Printing sheet according to claim 10, characterised in that pigment part of the top layer (1) comprises
  - a) 60 to 100 parts in dry weight, preferably 65 to 80 parts in dry weight of a fine particulate calcium carbonate with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,
  - b) 10 to 40 parts in dry weight, preferably 15 to 30 parts in dry weight of a fine particulate kaolin with a particle size distribution such that 95 % of the particles are smaller than 1  $\mu\text{m}$ ,
  - c) 10 to 15 parts in dry weight of a solid particulate polymer pigment with a particle size distribution centred at approximately 0.13 to 0.17  $\mu\text{m}$ , preferably centred at approximately 0.14  $\mu\text{m}$ , wherein 95 % of the particles are located within  $\pm 0.03 \mu\text{m}$  of this mean particle size.
13. Printing sheet according to one of the claims 10 or 12, characterised in that the solid particulate polymer pigment (c) is selected from the group consisting of: poly(methyl methacrylate), poly(2-chloroethyl methacrylate), poly(isopropyl methacrylate), poly(phenyl methacrylate), polyacrylonitrile, polymethacrylonitrile, polycarbonates, polyetheretherketones, polyimides, acetals, polyphenylene sulfides, phenolic resins, melamine resins, urea resins, epoxy resins, polystyrene latexes, polyacrylamides, and alloys, blends, mixtures and derivatives thereof.
14. Printing sheet according to one of the claims 10 to 13, characterised in that the solid particulate polymer pigment (c) is a modified polystyrene latex.
15. Printing sheet according to one of the claims 10 to 14, characterised in that the solid particulate polymer pigment (c) is based on styrene maleic acid copolymeric latexes (SMA) and/or styrene malimide copolymeric latexes (SMI),

preferably based almost exclusively on styrene malimide copolymeric latexes (SMI) with glass transition temperatures in the range of 200 °C.

16. Printing sheet according to one of the claims 10 to 15, characterised in that the binder part of the top layer (1) comprises

a') a binder selected from the group consisting of latex, in particular styrene-butadiene, styrene-butadiene-acrylonitrile, styrene-acrylic, styrene-butadiene-acrylic latexes, starch, polyacrylate salt, polyvinyl alcohol, soy, casein, carboxymethyl cellulose, hydroxymethyl cellulose and mixtures thereof,

b') additives like defoamers, colorants, brighteners, dispersants, thickeners, water retention agents, preservatives, crosslinkers, lubricants and pH control agents.

17. Printing sheet according to claim 16, characterised in that the binder is an acrylic ester copolymer based on butylacrylate, styrene and acrylonitrile.

18. Printing sheet according to one of the claims 16 to 17, characterised in that 10 to 16 parts in dry weight, preferably 11 to 14 parts in dry weight of binder (a') is present in the binder part.

19. Printing sheet according to one of the claims 10 to 18, characterised in that the top layer (1) has a total dried coat weight of in the range of 3 to 25 g/m<sup>2</sup>, preferably in the range of 4 to 15 g/m<sup>2</sup>, and most preferably of about 6 to 12 g/m<sup>2</sup>.

20. Printing sheet according to one of the claims 10 to 19, characterised in that the

image receptive coating layer has a second layer (2) beneath said top layer (1) comprising:

a pigment part, wherein this pigment part is composed of

A) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,

B) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 50 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution that more than 60 % of the particles are smaller than 1  $\mu\text{m}$ , or alternatively of a fine particulate carbonate with a particle size distribution such that more than 70% of the particles are smaller than 1  $\mu\text{m}$ ,

and a binder part, wherein this binder is composed of:

A') less than 20 parts in dry weight of binder and

B') less than 4 parts in dry weight of additives.

21. Printing sheet according to claim 20, characterised in that the pigment part of the second layer (2) comprises

A) 70 to 90 parts in dry weight, preferably approx. 75 parts in dry weight of a fine particulate calcium carbonate with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,

B) 20 to 40 parts in dry weight, preferably approx. 25 parts in dry weight of a fine particulate kaolin with a particle size distribution such that 65 % of the particles are smaller than 1  $\mu\text{m}$  or alternatively 50 to 70 parts of a fine particulate carbonate with a particle size distribution such that more than 70% of the particles are smaller than 1  $\mu\text{m}$ .

22. Printing sheet according to one of the claims 20 to 21, characterised in that the binder part of the second layer (2) comprises
- A') a binder selected from the group consisting of latex, in particular styrene-butadiene, styrene-butadiene-acrylonitrile, styrene-acrylic, styrene-butadiene-acrylic latexes, starch, polyacrylate salt, polyvinyl alcohol, soy, casein, carboxymethyl cellulose, hydroxymethyl cellulose and mixtures thereof,
- B') additives like defoamers, colorants, brighteners, dispersants, thickeners, water retention agents, preservatives, crosslinkers, lubricants and pH control agents.
23. Printing sheet according to claim 22, characterised in that the binder is an acrylic ester copolymer based on butylacrylate and styrene.
24. Printing sheet according to one of the claims 20 to 23, characterised in that 6 to 20 parts in dry weight, preferably 8 to 14 parts in dry weight, and most preferably approximately 10 parts in dry weight of binder is present in the binder part (A') of the second layer (2).
25. Printing sheet according to one of the claims 20 to 24, characterised in that the second layer (2) has a total dried coat weight of in the range of 5 to 25 g/m<sup>2</sup>, preferably in the range of 8 to 20 g/m<sup>2</sup>.
26. Printing sheet according to one of the claims 20 to 25, characterised in that beneath the second layer (2) there is a third layer (3) which is composed of a pigment part, wherein this pigment part is composed of

AA) 50 to 100 parts in dry weight of a particulate carbonate with a particle size distribution such that more than 70 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately or more than 80 % of the particles are smaller than 1  $\mu\text{m}$ , and a binder part, wherein this binder is composed of:

AA') less than 10 parts in dry weight of binder and

BB') less than 4 to 6 parts in dry weight of additives.

27. Printing sheet according to one of the preceding claims, characterised in that its total weight is in the range of 90 or 100 to 250  $\text{g/m}^2$  or up to 400  $\text{g/m}^2$ .
28. Printing sheet according to one of the preceding claims, characterised in that the substrate (5) is provided with an image receptive coating on both sides.
29. A method of manufacturing a printing sheet comprising:
  - dd) applying an image receptive top of layer (1) on the substrate said top layer (1) comprising:
    - a pigment part, wherein this pigment part is composed of
      - a) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,
      - b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 90 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution that more than 95



% of the particles are smaller than 1  $\mu\text{m}$ ,

c) 0 to 20 parts or up to 30 parts in dry weight of a particulate, preferably solid or vacuolated polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than 0.5  $\mu\text{m}$ , preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3  $\mu\text{m}$ , in particular between 0.1 and 0.2  $\mu\text{m}$ , or in the case of a vacuolated polymer pigment also with a mean particle size of about 0.6  $\mu\text{m}$ , wherein optionally the particulate polymer pigment may replace the inorganic pigments (a,c) completely or partially,

and a binder part, wherein this binder part is composed of:

a') less than 10 parts in dry weight of binder and

b') less than 2 parts in dry weight of additives

ee) drying the image receptive coating layer

ff) calendering at a nip pressure of less than 200 N/mm at a temperature of less than 80 degrees Celsius.

30. A method according to claim 29, wherein the top layer (1) has a total dried coat weight of in the range of 3 to 25  $\text{g/m}^2$ , preferably in the range of 4 to 15  $\text{g/m}^2$ , and most preferably of about 6 to 12  $\text{g/m}^2$ .

31. A method according to one of the claims 29 or 30, characterised in an image receptive coating and in particular a top layer according to one of the claims 1 to 17.

32. A method according to one of the claims 29 to 31, characterised in that prior to the application of the top coat layer (1)

cc) a second layer (2) is applied on the substrate, said second layer (2) beneath

said top layer (1) comprising preferentially:

a pigment part, wherein this pigment part is composed of

A) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 1  $\mu\text{m}$ ,

B) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 60 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution that more than 70 % of the particles are smaller than 1  $\mu\text{m}$ , or alternatively of a fine particulate carbonate with a particle size distribution such that more than 70% of the particles are smaller than 1  $\mu\text{m}$ ,

and a binder part, wherein this binder is composed of:

A') less than 20 parts in dry weight of binder and

B') less than 4 parts in dry weight of additives

33. A method according to claim 32, wherein the second layer (2) has a total dried coat weight of in the range of 5 to 25  $\text{g/m}^2$ , preferably in the range of 8 to 20  $\text{g/m}^2$ .
34. A method according to one of the claims 32 or 33, characterised in a second layer (2) according to one of the claims 19 to 24.
35. A method according to one of the claims 32 to 34, characterised in that prior to the application of the second layer (2)
  - bb) a third layer (3) is applied on the substrate, said third layer (3) beneath said second layer (2) comprising:

AA) 50 to 100 parts in dry weight of a particulate carbonate with a particle size distribution such that more than 70 % of the particles are smaller than 1  $\mu\text{m}$ , preferably with a particle size distribution such that approximately or more than 80 % of the particles are smaller than 1  $\mu\text{m}$ ,

and a binder part, wherein this binder is composed of:

AA') less than 10 parts in dry weight of binder and

BB') less than 4 to 6 parts in dry weight of additives.

36. A method according to claim 35, characterised in that prior to the application of the third layer (3) a sizing layer (4) is applied to the substrate (5).
37. A method according to one of the claims 29 to 36, characterised in that the image receptive coating is applied on both surfaces of the substrate (5).
38. A method according to one of the claims 29 to 37, characterised in that the resulting printing sheet has a total weight in the range of 80 to 400  $\text{g/m}^2$ , preferentially of 100 to 250  $\text{g/m}^2$  after the coating process.
39. A method according to one of the claims 29 to 38, characterised in that in the calendering step (ff) a nip pressure of in the range of 60 to 150 N/mm, preferentially of 90 to approximately 110 N/mm is being used.
40. A method according to one of the claims 29 to 39, characterised in that in the calendering step (ff) a temperature of in the range of 45 to 80 degree Celsius, preferably in the range of 50 to 70 degree Celsius is being used.

41. A method according to one of the claims 29 to 40, characterised in that 4 nips or less are being used in the calendering step (ff).
42. A method according to one of the claims 29 to 41, characterised in that in the calendering step (ff) rolls of steel or fibre surface are being used at a speed of 300 to 1000 m/min.
43. A method according to one of the claims 29 to 41, characterised in that prior to the calendering (ff) of the printing sheet is dried to a moisture of less than 5%.
44. Use of a printing sheet according to one of the claims 1 to 28 in an offset printing process.